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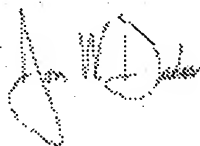
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Acting Under Secretary of Commerce  
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**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**  
 This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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<b>INVENTOR(S)</b>		<b>Residence</b> (City and either State or Foreign Country)	
Given Name (first and middle (if any))	Family Name or Surname	Fairbanks, Alaska	
Hajo	Eicken		
Additional inventors are being named on the _____ separately numbered sheets attached hereto			
<b>TITLE OF THE INVENTION (500 characters max)</b>			
Application of an Organic Polymer to Alter Microstructure and Decrease Strength of Saline Ice			
<b>CORRESPONDENCE ADDRESS</b>			
Direct all correspondence to:			
<input type="checkbox"/> Customer Number	<div style="border: 1px solid black; width: 150px; height: 30px; margin: 0 auto;"></div> Type Customer Number here		
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<b>ENCLOSED APPLICATION PARTS (check all that apply)</b>			
<input checked="" type="checkbox"/> Specification	Number of Pages	11	<input type="checkbox"/> CD(s), Number
<input type="checkbox"/> Drawing(s)	Number of Sheets		<input type="checkbox"/> Other (specify)
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76			
<b>METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT</b>			
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.		<b>FILING FEE AMOUNT (\$)</b> <div style="border: 1px solid black; width: 80px; height: 40px; margin: 0 auto; text-align: center;">\$80.00</div>	
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<input type="checkbox"/> No.		National Science Foundation	
<input checked="" type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are:		NSF-OPP 0085457	

Respectfully submitted,

SIGNATURE

*K. D. McLean*

TYPED or PRINTED NAME K. Diane McLean

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Date 7/8/03

REGISTRATION NO.

(If appropriate)  
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**USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT**  
 This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop Provisional Application, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.  
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INVENTOR(S)/APPLICANT(S)		
Given Name (first and middle (if any))	Family or Surname	Residence (City and either State or Foreign Country)
Christopher	Krembs	Seattle, Washington

[Page 2 of 2]

Number 2 of 2

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**Technology Disclosure****Title of technology:**

Application of an organic polymer to alter microstructure and decrease strength of saline ice

**Contributors:**

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**Research grants supporting this work:**

Title: Collaborative LExEn Research on the Role of Exopolymers in Arctic Sea Ice: Habitat Alteration and Microbial Cryoprotection

Sponsor: National Science Foundation, Office of Polar Programs

Grant no.: NSF-OPP 0085457

Investigators: Deming (UW), Eicken (UAF), Krembs (UW)

**Dates of conception and public disclosure:**

- June 2001: First thoughts about practical applications and industrial use of findings
- so far no public disclosure in the form of publications, presentations or open discussions
- anticipated date of publication: submission of manuscript by September 2002

**Reduction to practice:**

So far, a reduction to practice has occurred to the extent that artificial ice sheets have been grown in an outdoor tank, simulating the natural environment, with detailed measurements demonstrating the substantial reduction in ice strength (see description of technology for details).

**Potential businesses interested in the technology****(1) Ice strength reduction:**

- Alyeska Pipeline Co (both for port installations as well as access to subterranean pipes in permafrost etc.)
- British Petroleum, Phillips Alaska and other oil companies involved in production in Arctic and Sub-Arctic environments (wide range of applications: reduction of stress on marine and offshore structures such as in Alaska, Caspian Sea and elsewhere, reduction of ice strength to allow access to pipes and other installations in marine environment, mitigation and access to pipelines in land-fast ice areas in case of oil spills etc.)
- Anchorage Port authority (plus other port authorities in seasonally frozen harbours)

**(2) Polymer for enhancement of cooling/pumping properties in binary ice mixtures (p. 10):**

- Integral Energytechnik, Lise-Meitner-Str. 2, Postfach 1910, D-24909 Flensburg, Germany, Phone: +49-(0)461-999 333, Fax +49-(0)461-999 399 (company director Dr.-Ing. Joachim Paul)

**(3) Fruit juice industry (reduction of polymer presence in fruit juice concentrates, p. 10):**

- MinuteMaid/Coca-Cola Corp. and other producers of fruit juice concentrates

## Description of technology

### Process and effects

The microstructure and physical properties of ice growing from seawater or other solutions containing dissolved impurities (electrolytes, organic matter etc.) under quiescent conditions can be modified substantially to suit industrial and engineering applications by adding Xanthan gum<sup>1</sup> (and possibly other types of organic polymers) to the water. While the effect of changes in water salinity and addition of inorganic ions on ice properties and microstructure is reasonably well understood (Wettlaufer, 1998; Eicken, 1998), the technology and application described here - to our knowledge - has not been considered previously and has a much more dramatic impact on ice microstructure and properties. Also, the microphysical principles underlying these effects have not been considered previously in this context and differ principally from those identified in previous research.

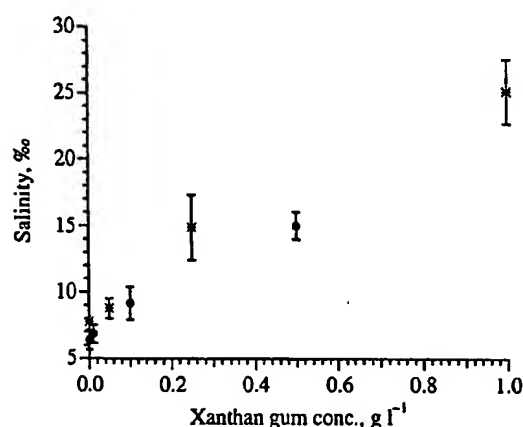


Figure 1a: Bulk ice salinity as a function of Xanthan gum concentration in parent water. Asterisks and solid dots denote first and second batch of experiments under different environmental conditions (growth rates). Vertical bars indicate the standard deviation of bulk salinities between three replicate samples.

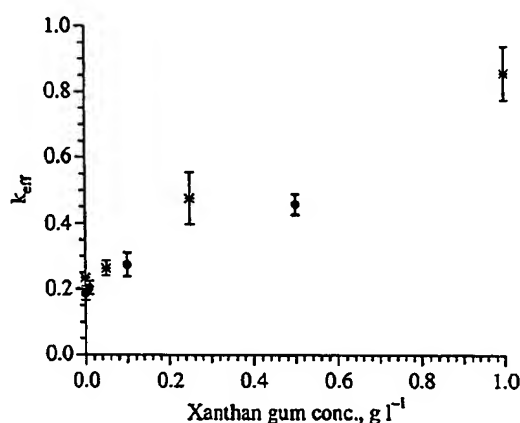


Figure 1b: Effective segregation coefficient  $k_{eff}$  determined from experiments summarized in Figure 1a.

An integral measure of the effect of Xanthan gum (XG) on ice growth and properties is shown in Figure 1a, indicating the increase in bulk ice salinity as a function of XG concentration for a set of outdoor experiments conducted under natural environmental conditions at the University of Alaska in Fairbanks<sup>2</sup>. For XG

<sup>1</sup> Xanthan gum is a natural product of a soil bacterium *Xanthomonas campestris*.

<sup>2</sup> Two sets of experiments were conducted by growing NaCl ice in four 200 l insulated tanks placed outside in Feb/March 2002 with ambient temperatures ranging between about -30 and -5 °C. Xanthan gum was added to three of these tanks in each experiments at concentrations 0.01, 0.05, 0.1, 0.25, 0.5 and 1 g l<sup>-1</sup>, and a control without additives. A pressure relief mechanism prevented build-up of pressure within tank during ice growth. Ice thickness was measured twice daily and the experiment terminated after an ice thickness of approximately 0.15 m had been reached within a week. Three sets of replicate samples (10 x

concentrations of about  $0.5 \text{ g l}^{-1}$  (in the parent water mass), salinity of the ice is increased by more than a factor of two. In terms of an effective segregation coefficient  $k_{\text{eff}}$ , describing the ratio between the salt concentration in the ice to that in the bulk water ( $k_{\text{eff}} = S_i/S_w$ ), the values determined here range between about 0.24 and 0.85 at growth velocities of about 1 to  $2.5 \text{ cm day}^{-1}$ . There are three important novel aspects to this finding. First, the segregation coefficient of 0.85, to our knowledge, is the highest measured and reported so far (Figures 1b and 2) for any type of saline ice. At the same time it is at least twice as high as values typically found in natural sea ice under rapid growth conditions. Second, while the segregation coefficients for control runs without XG additive are comparable to standard values (Weeks and Ackley, 1986), the addition of XG results in an increase in  $k_{\text{eff}}$  at growth velocities of up to an order of magnitude lower than required for comparable effects without XG additive (Figure 2). As the method employed here to determine segregation coefficients is likely to underestimate the magnitude of  $k_{\text{eff}}$  to some degree, these values can be considered conservative estimates of the impact of XG on ice salinity. Third, as vertical salinity profiles and theoretical considerations demonstrate, the reduction in molecular diffusivities and the increase in brine viscosity due to the presence of XG (e.g., Marcotte et al., 2001) not only impact the segregation of salts at the ice-water interface but also drastically reduce later desalination of the ice, thus greatly prolonging the impact of the additive as compared to other additives which are continually being lost from the ice during ageing.

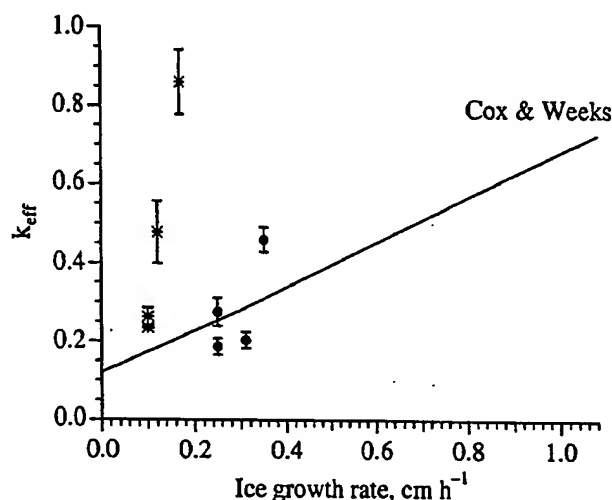


Figure 2: Segregation coefficient  $k_{\text{eff}}$  vs. ice growth rate for different experiments. Asterisks and dots denote first and second batch of experiments conducted at different growth rates. Vertical bars indicate standard deviation for set of three replicate samples. The solid line indicates the growth rate dependence and maximum value determined in laboratory experiments on artificial NaCl ice by Cox and Weeks (1975). Note that the increase in segregation coefficients as a result of addition of Xanthan gum occurs at much lower growth rates than the maximum values observed for ordinary NaCl ice.

10 cm in cross-section) were obtained from each tank, sectioned into 2.5 cm thick slices for measurements of salinity and XG concentration. Vertical and horizontal thin sections were cut and photographed as described by Eicken (1998).

The thin-section images shown in Figures 3 and 4 demonstrate that the ice undergoes profound changes in microstructure as well, with pore sizes and pore connectivity increasing substantially and further impacts on grain microstructure. Based on in-situ ice temperature and salinity measurements the in-situ liquid (brine) pore volume fraction  $V_p/V$  has been derived according to the method described by Cox and Weeks (1983). The brine porosity of ice grown from water with XG additive is thus higher by a factor of more than two. As corroborated by microstructural pore analysis, this increase in porosity represents a conservative estimate because the method of computing in-situ brine volumes does not account for the additional impact of XG on the pore space. Furthermore, for very thin ice, differences in ice temperature due to different thickness also result in an underestimation of the increase in porosity under full-scale, natural conditions.

As ice porosity and microstructure are key parameters controlling the physical properties of sea ice on macroscopic all the way to the largest of scales (Eicken, submitted), the addition of XG has a substantial impact on the properties and large-scale behaviour of saline ice in different environments. While we surmise that many of these impacts have industrial or engineering applications (and these are discussed in more detail below), one of the most pronounced impacts is on ice strength. Figure 5 highlights this by showing the low overall yield strength and highly ductile mode of failure of ice grown at XG concentrations of  $0.5 \text{ g l}^{-1}$ . In comparison with ordinary saline ice which can only be fragmented with great difficulty, the ice grown from water with XG additive has the same large-scale morphology and plate appearance but is easily crushed to a slushy pulp.

While it will require dedicated measurements of ice strength using methods adapted to the different ice rheology, some measure of the impact on ice strength due solely to the increase in brine porosity can be assessed from computation of ice tensile strength  $\sigma_t$ , based on a simple structural model, as described in detail by Weeks and Ackley (1986). It needs to be pointed out, however, that this model assumes a "standard" microstructure and does not account for the significant reduction in ice strength due to the microstructural changes apparent in Figures 3 and 4 which also affect the mode of failure, hence significantly underestimating the impact of XG. Nevertheless, from Figure 5 it is apparent that the addition of 0.5 and 1 g XG  $\text{l}^{-1}$  liquid reduces ice strength (both the maximum value in the profile as well as the strength in the neutral fiber) by a factor of more than 2.



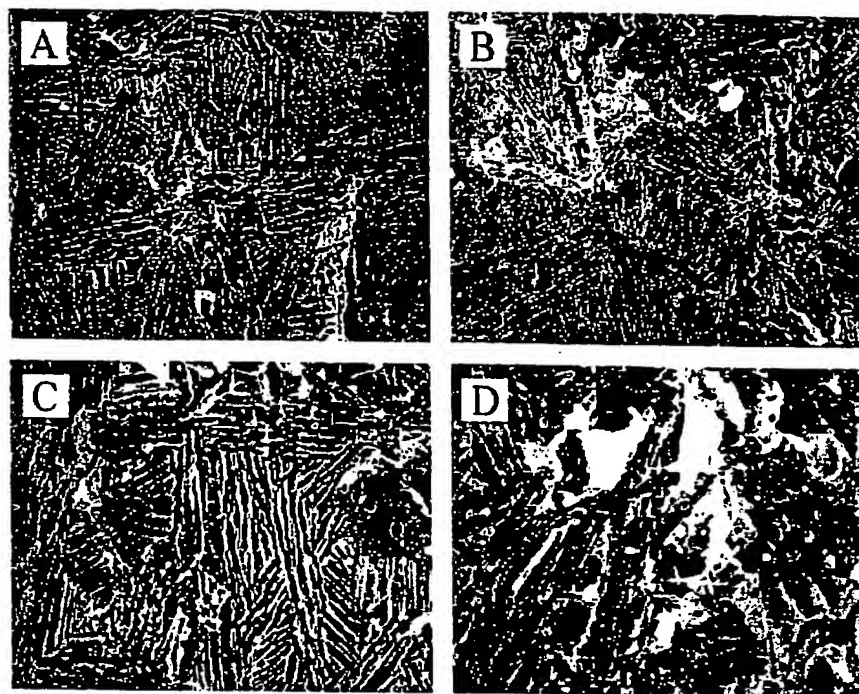


Figure 3: Pore microstructure of ice grown at different XG concentrations (A:  $0 \text{ g l}^{-1}$ , B:  $0.01 \text{ g l}^{-1}$ , C:  $0.1 \text{ g l}^{-1}$ , D:  $0.5 \text{ g l}^{-1}$ ). The horizontal thin sections are 50 mm wide and were obtained at approximately 9 cm depth in the ice cover. They show the in-situ pore distribution as evident from injection of a white contrast agent into pores. Note the differences in total porosity, pore size and connectivity. Ice salinities for the corresponding layers are A: 8.1 ‰, B: 8.2 ‰, C: 11.7 ‰, D: 19.4 ‰.

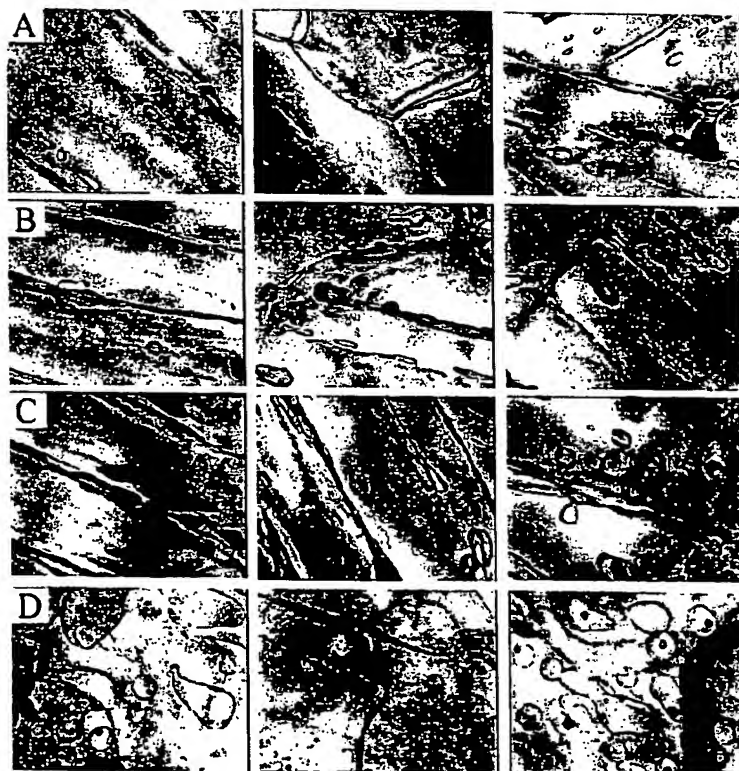


Figure 4: Microphotographs of pore microstructure of ice identical to that in Figure 3 but lacking contrast agent. (A:  $0 \text{ g l}^{-1}$ , B:  $0.01 \text{ g l}^{-1}$ , C:  $0.1 \text{ g l}^{-1}$ , D:  $0.5 \text{ g l}^{-1}$ ). The horizontal micrographs are 0.235 mm wide and were obtained at approximately 9 cm depth in the ice cover. Brine inclusions appear dark with ice transparent/light. Note the differences in microstructure, increasing with XG concentration. Ice salinities for the corresponding layers are A: 8.1 ‰, B: 8.2 ‰, C: 11.7 ‰, D: 19.4 ‰.

### Applications and deployment techniques in the context of lowering ice strength

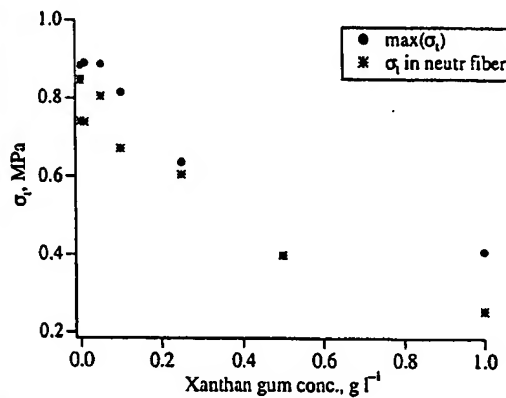
The addition of a suspension of Xanthan gum to growing ice does not prevent its formation but drastically softens the ice to a degree that it can be kneaded with bare hands (Figure 5). One obvious application of this effect is to soften ice in the natural environment where advantageous for engineering or industrial tasks. This would include the introduction of XG into surface waters at the onset of fall freeze-up and during winter ice growth in cold region harbours or other marine installations (Figure 6). Such procedure would allow for operations in these waterways during the course of winter without restrictions or damage due to solid ice. It would furthermore significantly reduce or abate potential damage due to build-up of ice internal stresses that are known to cause substantial, recurring damage to structures in important waterways.



A



B



C

Figure 5: Demonstration of ductile failure and low yield strength of ice grown from water with XG concentration of 0.5 g l<sup>-1</sup> (ice temperature -4.6 to -6.2 °C). Note how originally intact ice (A) completely disintegrates upon effortless kneading by hand (B). Figure 5 C illustrates reduction in ice tensile strength  $\sigma_t$  solely due to increase in porosity (for details see text).

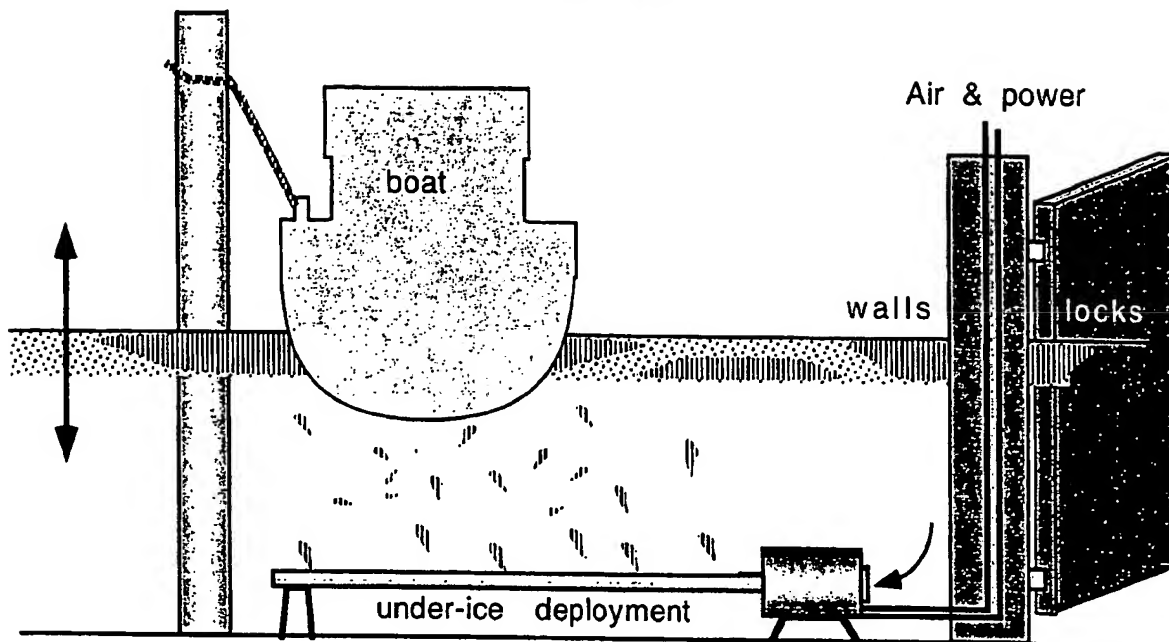


Figure 6: Schematic depiction of deployment and distribution of Xanthan gum emulsion in an application to reduce ice strength and stresses upon vessels, pilings and port installations.

The advantages of XG deployment are numerous in this context, some of them being: (1) As XG does not prevent ice formation, the insulating properties of an ice cover are still maintained (with better insulating properties due to entrainment of gas bubbles and reduced brine drainage). Thus, heat loss from a water body is actually minimized, reducing the total amount of ice formed and at the same time reducing moisture fluxes which would otherwise lead to fog and icing problems. Similarly, from a defense-strategic perspective, the application of XG would reduce ice strength while giving the appearance of port facilities being completely ice-locked. (2) In contrast with other additives that affect the freezing point of water through colligative properties, requiring massive amounts of potentially harmful substances (Roe and Polizzotti, 1992), XG is highly effective even at very low concentrations ( $<1 \text{ g l}^{-1}$ , as compared to, e.g., tens to hundreds of grams per liter for glycol-based freezing-point depressants). (3) At the same time, XG is safe for the environment (as attested by its prolific use as a food additive, e.g., Igoe, 1982) and biodegradable. (4) XG has lubricating effects (utilized, e.g., as a drilling fluid additive) which further reduce resistance to structures or vessels in iced waters.

A further, most significant trait of XG forms the basis for the mode of its deployment and application that is an integral part of the technological approach described here. XG can easily be emulsified even at low concentrations, with a bubbler device injecting Xanthan gum foam and possibly other additives that positively impact the properties of the emulsion (salts, anti-fouling agents, corrosion inhibitors, etc.). Thus, the preferred method of deployment would be emulsification of seawater pumped in-situ at the bottom or at mid-water level, mixed with air from an above-ground intake and dispensed through a rotating arm or series of mobile or fixed pipes. The air bubbles retained within the viscous fluid would induce the emulsion to float up under the ice and bring it into direct contact with the ice water interface, where its effect is strongest. Owing to the significant reduction in molecular diffusivities of gases and dissolved

matter in such emulsified water, additives as well as air bubbles can be maintained at higher concentrations for significant periods of time. Furthermore, build-up of XG under the ice in the laminar boundary layer further minimizes loss due to turbulent shear and advection.

Based on the same principles, XG can also be used to great advantage in on-land applications where one seeks to minimize damage due to freezing of surface layers in both seasonally cold and permafrost regions. Here, adding a slurry of XG and water (of a salinity that corresponds to the in-situ soil salinity) can prevent freeze-damage of pipes, ensure access to buried structures even in the coldest part of the season while at the same time acting as an in-situ lubricant.

### **Differences between the present technology and existing patents**

As outlined above, the present approach is novel in several ways. Research in the US Patent and Trademark Office on-line data base yielded few other patents that address the use of polymers in the context of ice strength and adhesion. While this research needs to be deepened and assessed by a professional with expertise in patent law, none of these previous techniques address methods to reduce bulk ice strength with a polymer in the environment. One proposes a solid, water-insoluble polymer coating on particles to prevent coagulation and freezing of particle mixtures with the possible admixing of anti-freeze agents (Kestner and Stoldt, 1981; Roe and Polizzotti, 1992), while others propose addition of colligative freezing-point depressants such as salt solutions or water soluble organic compounds such ethylene glycol to reduce the amount and strength of ice bonding coarser particles. The most relevant of these patents appears to be that of Roe (1984), who proposes use of a cationic polymer (gelatin or ammonium-based compounds) to enhance the retention of freezing-point depressants within an aggregation of coal particles at low temperatures. However, that technology does not rely on implicit properties of organic polymers in reducing macroscopic ice strength but rather uses polymers to reduce wash-out of water soluble freezing-point depressants. Furthermore, its application is limited to coal with moisture contents typically <5 %. Polymer weight fractions in water are also one to two orders of magnitude higher than those employed in the present technology before an effect is observed. The reduction in ice-bonded coal aggregate strength in the latter application ranges between 10 and 50 %.

### **Advantages and strengths**

Summarizing and extending the characteristics of the technology described above, the following advantages have been identified:

1. New application using principles not previously considered or understood
2. Cost and material effective, efficient at low concentrations at very low production costs
3. Easily prepared even in extreme environments and efficiently applied through bubble/emulsification process
4. Environmentally degradable at a rate slow enough to persist for months during the cold season but fast enough to prevent build-up during the warm season
5. Little dispersion or dilution in the environment due to high viscosity, and reduced molecular diffusivities of dissolved matter in the XG-water emulsion
6. Tendency to adhere to surfaces where its impact is greatest

7. Once incorporated into the ice, the desired effect persists for long time periods; due to greatly reduced desalination rates there is no need for re-application
8. As it does not act as freezing-point depressant, the softened ice can still maintain (and even improve) its insulating properties with beneficial environmental and strategic effects
9. Emulsified Xanthan gum foam can be used as an effective carrier of additives, stains, cryoprotectants etc. allowing specific design and retention of special desired properties
10. Potentially positive side effects with respect to reduction of biofouling
11. With increasing development of ports, offshore oil and gas terminals and other applications there is an increasing, as of yet completely untapped market in sub-Arctic and Arctic regions

### **Economic aspects**

With Xanthan gum being commercially available at prices of around \$6.60 per kg, and with one kilogram of XG yielding a very strong effect on ice strength at  $1 \text{ g l}^{-1}$  concentrations, with a statistically discernible impact at  $0.1 \text{ g l}^{-1}$ , for ideal deployment (i.e. no loss into the water) a strong effect could be achieved at \$ 3.30 per metric ton of sea ice with a discernible effect setting in at \$0.66 per metric ton. For a typical application, such as in a port with a surface area of  $0.1 \text{ km}^2$  and an ice thickness of 0.3 m, assuming an efficiency of 25 %, a single application would require \$54,000 worth of XG that should last over the entire length of a typical ice growth season in sub-Arctic and possibly Arctic latitudes. As seawater and air are taken in directly and emulsification can take place in-situ (Figure 6) the only other costs are those for installing and maintaining a relatively simple infrastructure. While \$54,000 is a substantial sum on its own, in comparison with typical costs part of icebreaker operation or seasonal ice-damage repair work this sum is one, if not two orders of magnitude smaller. Also, while traditional freezing-point depressants would not yield a comparable effect and harmfully impact the environment, one could calculate the costs associated with increasing ice porosity by the same amount, assuming the same efficiency (also unrealistic due to low viscosity and water solubility of candidate substances). For the same example, this would require approximately 500 metric tons of ethylene glycol, amounting to more than \$300,000.

### **Marketing aspects**

From a marketing perspective we see a number of potential applications, although we have not pursued any of them in any detail. A more specific range of potential products and services includes:

1. Large-scale applications at oil and gas terminal installations in seasonally or episodically ice-covered water (Valdez, Siberian gas tanker terminals); deployment either through surface spraying prior to freeze-up or injection of bubble-emulsion from below using rotary or mobile dispenser units (Figure 6)
2. Smaller-scale deployment along quays, pilings, in lock chambers, marinas and other installations to reduce or abate build-up of stress against installations due to ice growth and ice pressure

3. Large-scale applications in closed or semi-enclosed port basins, shipyard docks and other large marine enclosures allowing passage for vessels without full or any ice-strengthening
4. Introduction of anti-corrosion or fouling agents and other trace chemicals inducing desired effects in structures with Xanthan gum emulsion
5. Deployment in strategic harbors to produce "camouflage" ice that does not impede marine vessel traffic while giving the appearance of complete lock-up with ice and access to terrestrial vehicles
6. Deployment of polymer-water-brine mixtures into ground surface or other semi-enclosed terrestrial structures to prevent or abate freeze-damage to buried or half buried structures in seasonally frozen or permafrost regions

#### Further potential applications

In addition to the more specific applications and products outlined above, we feel that the present technology and derivatives may be of substantial importance in a variety of sectors. Two more specific examples include the following:

1. The phasing out of freon-based refrigerants has resulted in an increasing market for environmentally inert and harmless alternative refrigerants. One such technique widely employed is the use of ice-brine slurries for refrigeration applications ranging from food display cases in supermarkets to cooling of the railroad/car tunnel between the UK and France (Paul, 1993). The efficiency of the brine-ice coolant and the applicable temperature range increases with increasing ice content and increasing salinity. However, for commonly employed NaCl (and other inorganic salt) brines the minimum temperature that can be achieved is limited by the temperature at which the freezing-point depressant properties of the dissolved salt in the brine are overtaken by the tendency for salt to precipitate out of solution. For NaCl solutions, this absolute limit corresponds to the eutectic at  $-21.2^{\circ}\text{C}$  (Spencer et al., 1990). A further limitation is the fact that ice-brine slurries can only be pumped up to a critical ice volume fraction (typically 10 to 50 %) which further limits the cooling efficiency. While not tested under realistic conditions, we anticipate that the addition of Xanthan gum has three major, highly beneficial effects on the thermal and rheological properties of such ice-brine coolants. First, by allowing the retention of greater amounts of salt in an ice-brine mixture, XG reduces the likelihood of local stoppage and freeze-up of slurries even at higher ice volume fractions. At the same time, the reduction in strength of the ice slurry can be expected to greatly reduce or completely prevent the negative impacts of local freeze-up due to variations in temperature control (or allow for lower temperatures to be achieved in the coolant). Second, organic polymers have been demonstrated to depress the precipitation temperature of hydrohalite ( $\text{NaCl} \times 2 \text{H}_2\text{O}$ ) in experiments (Izutsu et al., 1995), thereby allowing further lowering of ice-brine slurry temperatures. Finally, organic polymers have been shown to significantly enhance turbulent mixing in pipe flow due to their non-Newtonian rheology (Groisman and Steinberg, 2001), thereby significantly increasing the efficiency of heat transfer between the cooling coils and the surrounding medium.
2. Fruit juice concentrates are often produced industrially through sequential freezing of raw, low-concentration juice (Miyawaki et al., 1998). Here, the efficiency of the concentration process depends strongly on the segregation coefficient applicable to ice grown in such juice-ice mixtures. While we have not researched this issue

thoroughly, it appears that the high concentrations of organic polymers in natural juices (in particular apple and citrus juices) may in fact have negative effects on the efficiency of concentrate extraction, possibly unbeknownst to the industry. Here, based on our work one could develop a method designed to either permanently or temporarily immobilizing organic polymers through heat treatment or FDA-approved chemical means.

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